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Trends in Auto Emissions and Gasoline Composition

by Robert F. Sawyer

The invention of the spark-ignited internal combustion engine provided a market for a petroleum middle distillate, gasoline, about 100 years ago. The internal combustion engine and gasoline have co-evolved until motor vehicles now annually consume about 110 billion gallons of gasoline in the United States. Continuing air pollution problems and resulting regulatory pressures are driving the need for further automotive emissions reductions. Engine and emissions control technology provided most earlier reductions. Changing the composition of gasoline will play a major role in the next round of reductions. The engineering and regulatory definition of a reformulated gasoline is proceeding rapidly, largely as the result of an auto and oil industry cooperative data generation program. It is likely that this new, reformulated gasoline will be introduced in high-ozone regions of the United States in the mid-1990s. Alternative clean fuels, primarily methane, methanol, and liquid petroleum gas, will become more widely used during this same period, probably first in fleet operations.

Historical Background

The commercial development of petroleum during the last half of the nineteenth century was motivated by the need for an inexpensive substitute for whale oil. Distillation of crude petroleum to produce kerosene for use as lamp oil left several byproducts for which there was no market, among them gasoline. This distillate proved better suited than kerosene for use in the then-developing spark-ignited internal combustion engine. The internal combustion engine thereby provided a second market for petroleum products and soon outstripped the demand for lamp oil. The internal combustion engine and gasoline co-evolved over the next 100 years, with primary emphasis on the improvement of power, efficiency, and drivability. Lead was added to gasoline in the 1930s to increase knock resistance, allowing higher compression ratios and greater efficiency.

The role of the automobile in air pollution was recognized in the 1950s, and the first emissions controls were initiated in the 1960s. These controls have focused primarily on the engine. They have revolutionized engine design, most notably through the introduction of computer control. The co-evolution of engine and fuel continued. Two important fuel modifications occurred: removal of lead from gasoline allowed use of catalytic after treatment, and reduction of gasoline vapor pressure assisted in the control of refueling and evaporative hydrocarbon emissions.

The emissions controls introduced in the 1970s were refined in the 1980s. Most importantly, the 1980s provided time for the needed turnover of vehicles necessary to nearly eliminate precatalyst vehicles from the motor vehicle fleet. As we enter the 1990s, the disappointing reality is that we are far from attaining air quality standards, especially in urban areas, and motor vehicles remain a major part of the problem. Increasing numbers of motor vehicles, miles traveled, and in-use emissions that exceed regulatory expectations prevent the attainment of expected emissions reductions. An additional effort to reduce in-use motor vehicle emissions reductions is necessary. The co-evolution of engines and fuels is continuing, but now the fuel is the focus of attention.

Gasoline

Gasoline is a middle distillate of petroleum, containing C_4 to about C_{12} hydrocarbons. Through catalytic and hydro cracking, modern refineries convert heavy distillates of petroleum into gasoline-blending components. Isomerization and reformation are employed to use light distillates as gasoline components. Practically all gasoline in the United States is made from petroleum. Tar sands, oil shale, and coal can be used as raw materials for gasoline, but they are not currently economically competitive with crude petroleum. Because of the extensive gasoline motor vehicle fleet and the gasoline production and distribution infrastructure, it is likely that gasoline will be the dominant motor vehicle fuel well into the next century, even as petroleum reserves are depleted.

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About 84% of the approximately 130 billion gallons of motor fuel consumed annually in the United States is gasoline (1). This gasoline fraction is much higher than for most countries in the rest of the world, where diesel fuel is much more widely used. The United States consumes about half of the world's gasoline. About 2 billion gallons of oxygenates, primarily ethanol and methyl *tert*-butyl ether (MTBE), are added to U.S. gasoline. As fuel economy and/or global warming concerns increase, a shift to a higher diesel motor fuel fraction in the United States is likely, but gasoline will remain the dominant fuel.

Regulatory Context

The Clean Air Act amendments of 1990 follow earlier Clean Air Acts in setting technology forcing emissions standards. They also establish a "clean fuel" program and require reformulated gasoline. California's right to set more stringent requirements and the option of other states that do not meet air quality standards to adopt the California motor vehicle emission standards is retained. The actions of the California Air Resources Board (CARB) therefore are significant not only in California but in other high-pollution states as well.

Emissions Regulations

More stringent national tailpipe emissions standards for automobiles are to be phased in over the 1994–1996 model years (Table 1). Durability requirements are doubled to 10 years or 100,000 miles. The EPA is directed to impose a second round of stricter tailpipe standards beginning in 2004 if needed, feasible, and cost effective. CARB has established requirements for low emission vehicles (LEVs) including zero-emission vehicles (ZEVs), which are electric vehicles (Table 2). The EPA and CARB propose new evaporative emission test methods designed to greatly reduce this source of hydrocarbon emissions. Additional new Clean Air Act requirements include a 10 g/mile carbon monoxide (CO) standard when tested at 20°F and on board diagnostics.

Reformulated Gasolines

The Clean Air Act amendments require reformulated gasoline in the nine cities that most seriously exceed ozone air quality standards beginning in 1995. This reformulated gasoline must decrease volatile organic compounds (VOCs) by 15%. It must also reduce toxics (benzene, 1,3-butadiene, formaldehyde, acetaldehyde, and polycyclic organic matter) by 15% in 1995 and 25% in 2000. A 2% year-round oxygen content is required. (A 2.7% winter oxygen content is required in cities out of CO attainment.) The EPA approach is based primarily on air quality improvement equivalence among different gasoline formulations. California is pursuing its own reformulated gasoline program, based primarily on fuel specifications (Table 3). The California LEVs would be certified on the California reformulated gasoline. Other states opting to receive California vehicles presumably would also adopt California reformulated gasoline, although this point is not clear.

Table 1. U.S. passenger car emission standards, 50,000 miles, Clean Air Act amendments of 1990.

Pollutant	1960 ^a	1989	1994–1996	2004 ^b
HC, g/mile	10.6	0.41	0.25 ^c	0.125 ^c
CO, g/mile	84.0	3.4	3.4	1.7
NO _x , g/mile	4.1	1.0	0.4	0.2
Evaporated HC, g/test	46.6	2.0	2.0 ^d	2.0 ^d

Abbreviations: HC, hydrocarbons; CO, carbon monoxide; NO_x, nitrogen oxides.

^aPrecontrol.

^bTo be reviewed by the administrator of the EPA.

^cNonmethane hydrocarbons.

^dNew test procedure.

Table 2. California Air Resources Board passenger car low-emission vehicle standards (g/mile).

Category	Year effective ^a	NMOG ^b	CO	NO _x
Current	1991	0.39	7.0	0.40
1993 Base	1993	0.25	3.4	0.40
TLEV	1995	0.125	3.4	0.40
LEV	1995	0.075	3.4	0.20
ULEV	1995	0.040	1.7	0.20
ZEV	1998	0.000	0.0	0.00

Abbreviations: NMOG, nonmethane organic gas; CO, carbon monoxide; NO_x, nitrogen oxides; TLEV, transition low emission vehicles; LEV, low-emission vehicles; ULEV, ultra low emission vehicles; ZEV, zero-emission vehicles.

^aIncludes phase-in, e.g., 10% ZEV in 2003.

^bStandards are adjusted for the photochemical reactivity of the fuel, e.g., methanol TLEV reactivity adjustment factor is 0.41.

Table 3. California Air Resources Board proposed reformulated gasoline specifications, producer limits.

Property	Limit ^a
RVP, psi	7.0
Sulfur, ppm	40
Benzene, vol%	1.0
Aromatics, vol%	25
Olefins, vol%	6
T-90, °F	300
T-50, °F	210
Oxygen, minimum weight%	1.8
Oxygen, maximum weight%	2.2

Abbreviations: RVP, Reid vapor pressure; T-90, 90% distillation temperature; T-50, 50% distillation temperature.

^aAveraging option also available with lower limits.

Alternative Fuels

The Clean-Fuel-Vehicle program of the Clean Air Act applies to 22 areas and fleet operations. Starting in 1998, vehicles with 80% lower emissions must be purchased. Clean fuels could be alternative fuels such as methanol, natural gas, or reformulated gasoline. Beginning in 1996, the industry must provide 150,000 clean-fuel cars and light trucks to California and in 1999, 300,000 vehicles. California, particularly the South Coast Air Quality Management District (2), has its own programs to promote the use of alternative fuels (Table 4).

Table 4. South Coast Air Quality Management District air quality management plan clean fuels strategy: motor vehicle miles traveled penetration assumptions for 2010 (2).

Vehicle class	% Use			
	Electric	Alternative fuels ^a	Gasoline	Diesel
Passenger cars	17	33	50	0
Light-duty trucks	9	38	53	0
Medium-duty vehicles	0	40	57	3
Heavy-duty vehicles	0	24	29	47
Urban buses	30	70	0	0
Locomotives	90	0	0	10

^aAlternative fuels under consideration include methanol, liquid petroleum gas, and natural gas.

Reformulated Gasoline

As now used, the term "reformulated gasoline" refers to gasoline blends designed to reduce emissions. That fuel composition affects emissions was known by early researchers and developers of vehicle emissions controls. Koehl et al. (3) review studies of the relations between fuel composition and emissions conducted over the past 30 years. Current interest is motivated, in part, by competition from clean alternative fuels such as alcohols, natural gas, and liquid petroleum gas.

Auto/Oil Program

Three domestic auto companies and fourteen petroleum companies established a cooperative testing and research program, the Auto/Oil Air Quality Improvement Research Program (AOP), to develop data on potential improvement in vehicle emissions and air quality from reformulated gasoline, other alternative fuels, and new automotive technology. Older (1983–1985), current (1989), and prototype vehicles are included. This \$40-million program is by far the most comprehensive and systematic study of the combined effects of fuel parameters on motor vehicle emissions. The resulting extensive database, now about 160 million entries, is publicly available.* Test results for a matrix of fuels, vehicles, and operating conditions include both exhaust and evaporative emissions data, including extensive hydrocarbon speciation (4–9).

Emissions Reductions

The AOP vehicle emissions data are based on Federal Test Procedure testing of a range of vehicles and fuels. ARCO used these data to guide its formulation of a reformulated fuel, EC-X (Table 5), which is similar to the CARB reformulated gasoline. ARCO selected this fuel from several tested as being the most cost effective, low-emission gasoline to produce. This fuel, when tested in a

Table 5. Industry average and ARCO EC-X reformulated gasoline (10).

Property	Industry average	EC-X
Octane (R + M)/2	86.8	90.0
RVP, psi	8.6	6.7
Sulfur, ppm	349	41
Benzene, vol%	1.0	0.7
Aromatics, vol%	34.4	21.6
Olefins, vol%	9.7	5.5
T-90, °F	323	293
MTBE, vol%	0.0	14.9

Abbreviations: R + M, road octane + motor octane; RVP, Reid vapor pressure; T-90, 90% distillation temperature; MTBE, methyl *tert*-butyl ether.

Table 6. ARCO EC-X reformulated gasoline emissions reductions (10).

Emission	Change, %
Total hydrocarbons	–31
Nonmethane organic gases	–36
Carbon monoxide	–26
Oxides of nitrogen	–26
Total toxics	–46
Evaporative hydrocarbons	–35

fleet of 1990 California vehicles, showed significant emissions reductions (Table 6). The magnitude and consistency of emissions reductions of chemical components is surprising (10).

Emissions reductions, air quality improvements, and regulatory requirements indicate that reformulated gasoline will be introduced in the 1990s. Presumably it will be required in, and allocated to, areas with the greatest ozone air-quality problems.

Alternative Fuels

Natural gas, methanol, liquid petroleum gas (LPG), ethanol, and hydrogen are the most likely alternatives as clean substitutes for gasoline. All are compatible with current gasoline and/or diesel engine designs, with modest modifications. Their relative attractiveness depends primarily on their air-quality improvement potential, which results primarily from lower photochemical reactivities. Availability and issues such as vehicle range and safety also are of concern.

Natural gas, methanol, and LPG are receiving the greatest attention. Natural gas is the cleanest and most widely available. Vehicle fueling, on-board storage, and range limitations should not impede the substantial adoption of natural gas as a motor fuel. Compared to natural gas, methanol is more like gasoline in its properties. Its proposed use as a blend with 15% gasoline (M-85) compromises emissions and air quality advantages compared with neat methanol (M-100), but solves cold start and safety problems. Widespread introduction of methanol would require greatly expanded production capability. The production of methanol from natural gas, the most likely feedstock, raises questions of energy efficiency and CO₂ emissions. LPG already is widely used internationally as a

*Information on obtaining Auto/Oil Program results, including the database on diskette, may be obtained by writing to the Coordinating Research Council, Inc., 219 Perimeter Center Parkway, Atlanta, GA 30346.

motor fuel, but its availability is very limited. Ethanol is widely used as a motor fuel in Brazil but does not offer the air quality advantages of the other fuels. Lack of availability precludes hydrogen, at least until an inexpensive, energy-efficient source is discovered.

Fuel Vapor Emissions

The emissions most directly associated with gasoline are fuel vapor emissions. These can be divided into two categories: storage and distribution emissions and vehicle evaporative emissions.

Storage and Distribution Emissions

At each point where gasoline is stored or transferred, the potential for fuel vapors to escape exists. During storage, fuel vapor pressure provides a driving force for the escape of hydrocarbon vapors, preferentially those having the highest vapor pressures, the low molecular weight compounds. Cyclic warming of the fuel vapor, changes in barometric pressure, and wind promote vapor emissions. Most storage tanks have provisions for minimizing emissions, such as floating roofs or vapor collection systems.

When a tank is filled with liquid, vapor is displaced and, if not collected, emitted to the atmosphere. Again, in most regions where ozone air quality is exceeded, these vapors are collected, for example, by the Phase II Vapor Recovery Systems now installed at many gasoline stations. If functioning properly, these systems effectively control emissions to the atmosphere and exposure to the person filling the automobile tank.

Vehicle Evaporative Emissions

Four recognized types of vehicle evaporative emissions are hot soak, diurnal, running losses, and resting losses. All are increased by fuel vapor pressure, altitude, and ambient temperature. Reduction of the fuel vapor pressure is an effective means to reduce emissions. The composition of these emissions is different from the fuel composition. Evaporative emissions are enriched in the low molecular weight species. Each type of evaporative emission has its own composition. Some example speciated compositions are provided in the appendix.

Hot soak emissions occur from the heating of the fuel system after engine shutdown. These occur primarily in carbureted vehicles. The increasing use of fuel injection is reducing the importance of the hot soak losses. These emissions, when occurring from vehicles parked in attached residential garages, contribute to indoor exposure.

Diurnal emissions result from the cyclic heating and cooling of the fuel tank. As the fuel and fuel vapor warm and expand, diurnal emissions leave the tank. The charcoal canister of the vehicle evaporative emission control system is designed to trap these emissions and to deliver them to the engine for destruction. If emissions exceed the capacity of the canister, vapors are emitted. Such emis-

sions can occur and can be aggravated if the vehicle is not operated. The temperature difference experienced by the fuel tank is an important parameter.

Running losses were recognized as a source of hydrocarbon emissions only about 2 years ago. In an extreme case, gasoline can be heated to the point that it boils in the fuel tank. Once the fuel boils, the evaporative emission control system is overwhelmed, and the engine may even be incapable of burning the vaporized fuel. Increasing engine temperatures, fuel tank design and location, and fuel injection (which heats and recirculates some of the fuel) all have increased the severity of these emissions. Reducing fuel volatility is an effective mitigation measure. Test methods and regulations are being established.

Resting losses result from the diffusion of fuel through plastic and rubber fuel system components and the escape of hydrocarbon vapors from the storage canister. These processes are not well understood. While emission rates are low, they occur continuously and in total can be significant. They are similar to hot soak emissions, but largely missed in the 1-hr hot soak test. Measurement of these emissions is difficult. The new California multiday evaporative test procedure beginning in 1995 will require control of these emissions. Speciated data are not yet available.

Exhaust Emissions

Fuel composition and many other engine and operating parameters affect the pollutant composition of the exhaust. Typically, 99.5–99.9% of engine exhaust from a modern, light-duty vehicle is nitrogen, carbon dioxide, and water vapor. The remainder contains the pollutants. Most important are hydrocarbons, aldehydes, carbon monoxide, oxides of nitrogen, and lead.

Hydrocarbons

Exhaust hydrocarbons can be raw fuel or modified in composition by the combustion process. The data in the appendix show that the hydrocarbon composition of fuel, evaporative emissions, and exhaust emissions are all different. The operating condition of the vehicle (cold start, hot stabilized, or hot start), also affects hydrocarbon composition.

Unburned gasoline can pass through the engine (for example, trapped in a crevice region) and catalyst (especially during cold start). Some of the exhaust hydrocarbon species therefore mimic the composition of the liquid fuel.

Pyrolysis products, which result from the high-temperature combustion environment and the catalytic reactor, can be species not present in the fuel. 1,3-Butadiene is an example of a hydrocarbon species found in the exhaust that is not present in the fuel. By monitoring the engine and tailpipe emissions composition, the role of the combustion and catalyst processes can be inferred. Such information, which is being generated by the AOP, is valuable to fuel, engine, and emission control designers.

Other Compounds

Aldehydes, carbon monoxide, oxides of nitrogen, and lead are also important exhaust emissions. Each is affected by the composition of the gasoline.

Aldehydes result from the partial oxidation of hydrocarbons or can be formed from oxygenated hydrocarbons contained in the fuel. Methanol and MTBE as fuel additives, for example, generally increase formaldehyde emissions. Ethanol and ethyl *tert*-butyl ether (ETBE) increase acetaldehyde emissions.

Carbon monoxide is an intermediate in the oxidation of hydrocarbons. The failure to fully convert carbon monoxide to carbon dioxide occurs primarily during cold start or results from an insufficiency of oxygen resulting from fuel-rich operation. A troublesome recent observation is that some vehicles go into a fuel-rich operating mode during heavy acceleration.

Oxides of nitrogen from gasoline vehicles result from the thermal fixation of atmospheric nitrogen. The process depends strongly on peak temperature and mixture ratio. The effect of fuel composition on oxides of nitrogen emissions is complex and not fully understood.

Lead emissions are the direct result of lead added to fuel as an antiknock agent. Atmospheric and human lead levels have fallen dramatically with the introduction of unleaded gasoline and reduction of lead levels in leaded gasoline. With the complete elimination of lead from gasoline, this problem will be solved.

Conclusions

Gasoline and the spark-ignition engine have co-evolved over the past 100 years. Additional changes are occurring, driven by the need to reduce further motor vehicle emissions. Gasoline composition and auto emissions are closely related. The mechanism of this relation is often complex, but new data are yielding a better understanding. Reformulated gasoline results in reduced emissions, is being

mandated by regulatory action, and should be introduced in the mid 1990s. This fuel will have a lower aromatic content (including specifically benzene), lower olefin content, an oxygenate additive, lower vapor pressure, reduced sulfur content, and reduced high-end (high molecular weight) content. Alternative "clean" fuels, primarily methane, methanol, and liquid petroleum gas, also can reduce emissions and are scheduled for introduction to fleet operations.

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Appendix

**Hydrocarbon composition of fuels and emissions: Hydrocarbon speciation of industry average gasoline,
EPA certification gasoline, and M-85 (85% methanol, 15% gasoline).^a**

CAS #	Compound	FUELS			EXHAUST EMISSIONS			EVAPORATIVE EMISSIONS			COMPSTE
		Ind Avg Gas	Cert Gas	M-85	Cold Start	Hot Stab	Hot Start	Diurnal	Hot Soak	Running Losses	
00074-82-8	Methane	0.000	0.000	0.000	0.0895	0.5446	0.2871	0.0078	0.0099	0.0084	0.1552
00074-85-1	Ethene	0.000	0.000	0.000	0.0790	0.0072	0.0522	0.0000	0.0000	0.0000	0.0269
00074-86-2	Ethyne	0.000	0.000	0.000	0.0376	0.0000	0.0000	0.0000	0.0000	0.0000	0.0087
00074-84-0	Ethane	0.000	0.000	0.000	0.0224	0.0411	0.0439	0.0006	0.0000	0.0000	0.0183
00050-00-0	Formaldehyde	0.000	0.000	0.000	0.0060	0.0298	0.0123				0.0080
00115-07-1	Propene	0.000	0.000	0.000	0.0397	0.0000	0.0101	0.0000	0.0000	0.0000	0.0107
00074-98-6	Propane	0.001	0.001	0.001	0.0000	0.0000	0.0000	0.0027	0.0004	0.0000	0.0004
00463-49-0	Propadiene	0.000	0.000	0.000	0.0013	0.0000	0.0000	0.0000	0.0000	0.0000	0.0003
00074-99-7	Propyne	0.000	0.000	0.000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
00075-28-5	2M-Propane	0.083	0.086	0.016	0.0004	0.0000	0.0018	0.0230	0.0035	0.0231	0.0092
00075-07-0	Acetaldehyde	0.000	0.000	0.000	0.0035	0.0216	0.0071				0.0054
00115-11-7	2M-Propene	0.014	0.015	0.000	0.0176	0.0000	0.0000	0.0000	0.0000	0.0000	0.0041
00106-98-9	1-Butene	0.000	0.000	0.000	0.0034	0.0000	0.0000	0.0000	0.0000	0.0000	0.0008
00106-99-0	1,3-Butadiene	0.000	0.000	0.000	0.0068	0.0000	0.0000	0.0000	0.0000	0.0000	0.0016
00106-97-8	Butane	4.650	4.085	1.012	0.0349	0.0665	0.0931	0.5270	0.2116	0.7337	0.2953
00624-64-6	t-2-Butene	0.001	0.001	0.000	0.0038	0.0000	0.0000	0.0000	0.0000	0.0000	0.0009
00463-82-1	2,2-DM-Propane	0.034	0.067	0.000	0.0006	0.0000	0.0000	0.0004	0.0000	0.0019	0.0006
00107-00-6	1-Butyne	0.000	0.000	0.000	0.0000	0.0000	0.0000	0.0000	0.0033	0.0000	0.0003
00590-18-1	c-2-Butene	0.004	0.001	0.000	0.0016	0.0000	0.0023	0.0000	0.0006	0.0000	0.0008
00563-45-1	3M-1-Butene	0.021	0.016	0.000	0.0000	0.0000	0.0000	0.0003	0.0000	0.0000	0.0000
00064-17-5	Ethanol	0.000	0.000	0.000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
00078-78-4	2M-Butane	4.417	2.306	0.567	0.0294	0.0458	0.0594	0.1030	0.0918	0.0888	0.0660
00503-17-3	2-Butyne	0.000	0.000	0.000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
00109-67-1	1-Pentene	0.146	0.114	0.019	0.0008	0.0000	0.0000	0.0019	0.0016	0.0017	0.0010
00563-46-2	2M-1-Butene	0.319	0.244	0.042	0.0020	0.0000	0.0008	0.0060	0.0058	0.0030	0.0026
00109-66-0	Pentane	3.385	1.212	0.440	0.0219	0.0123	0.0364	0.0521	0.0669	0.0317	0.0329
00078-79-5	2M-1,3-Butadiene	0.013	0.003	0.001	0.0017	0.0000	0.0000	0.0000	0.0007	0.0000	0.0005
00646-04-8	t-2-Pentene	0.617	0.384	0.083	0.0037	0.0000	0.0000	0.0094	0.0124	0.0032	0.0040
00558-37-2	3,3-DM-1-Butene	0.010	0.002	0.001	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
02738-19-4	2M-2-Hexene	0.338	0.205	0.051	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
03899-36-3	3M-t-3-Hexene	0.000	0.000	0.000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
14686-13-6	t-2-Heptene	0.131	0.078	0.019	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
00816-79-5	3E-c-2-Pentene	0.061	0.035	0.009	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
00107-89-1	2,4,4-TM-1-Pentene	0.104	0.061	0.016	0.0000	0.0000	0.0000	0.0000	0.0004	0.0000	0.0000
10574-37-5	2,3-DM-2-Pentene	0.000	0.000	0.000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
06443-92-1	c-2-Heptene	0.121	0.073	0.018	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
00108-87-2	M-Cyclohexane	0.542	0.285	0.081	0.0023	0.0000	0.0000	0.0000	0.0013	0.0000	0.0007
00590-73-8	2,2-DM-Hexane	0.063	0.032	0.008	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
00107-40-4	2,4,4-TM-2-Pentene	0.011	0.000	0.000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
00592-13-2	2,5-DM-Hexane	0.552	0.702	0.081	0.0034	0.0000	0.0000	0.0000	0.0011	0.0014	0.0012
01640-89-7	E-Cyclopentane	0.074	0.043	0.011	0.0005	0.0000	0.0000	0.0000	0.0000	0.0000	0.0001
00589-43-5	2,4-DM-Hexane	0.707	0.885	0.103	0.0051	0.0000	0.0009	0.0000	0.0014	0.0017	0.0018
00563-16-6	3,3-DM-Hexane	0.192	0.104	0.027	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
00565-75-3	2,3,4-TM-Pentane	2.157	3.288	0.255	0.0129	0.0000	0.0082	0.0030	0.0083	0.0066	0.0069
00108-88-3	Toluene	5.518	6.743	0.934	0.0754	0.0347	0.0588	0.0470	0.1363	0.0109	0.0528
00584-94-1	2,3-DM-Hexane	0.539	0.575	0.078	0.0029	0.0000	0.0014	0.0000	0.0012	0.0000	0.0010
00592-27-8	2M-Heptane	0.931	0.505	0.130	0.0048	0.0000	0.0014	0.0000	0.0015	0.0000	0.0014
00589-53-7	4M-Heptane	0.462	0.268	0.063	0.0013	0.0000	0.0008	0.0000	0.0000	0.0000	0.0004
00589-81-1	3M-Heptane	1.187	0.642	0.165	0.0079	0.0000	0.0029	0.0008	0.0027	0.0000	0.0026
15890-40-1	1c,2t,3-TM-Cyclopentane	0.000	0.000	0.000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
00638-04-0	c-1,3-DM-Cyclohexane	0.087	0.049	0.013	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
02207-04-7	t-1,4-DM-Cyclohexane	0.136	0.077	0.019	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
03522-94-9	2,2,5-TM-Hexane	0.519	0.642	0.081	0.0026	0.0000	0.0008	0.0000	0.0003	0.0000	0.0007
00111-66-0	1-Octene	0.075	0.041	0.011	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
14850-23-8	t-4-Octene	0.100	0.074	0.015	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
00111-65-9	Octane	0.856	0.429	0.119	0.0050	0.0000	0.0012	0.0000	0.0019	0.0000	0.0015
13389-42-9	t-2-Octene	0.074	0.043	0.011	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
02207-03-6	t-1,3-DM-Cyclohexane	0.125	0.079	0.019	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
07642-04-8	c-2-Octene	0.037	0.021	0.007	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
01069-53-0	2,3,5-TM-Hexane	0.103	0.111	0.016	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
02213-23-2	2,4-DM-Heptane	0.171	0.103	0.025	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
02207-01-4	c-1,2-DM-Cyclohexane	0.148	0.093	0.023	0.0000	0.0000	0.0000	0.0035	0.0000	0.0000	0.0005

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Appendix. Continued.

CAS #	Compound	FUELS			EXHAUST EMISSIONS			EVAPORATIVE EMISSIONS			COMPSTE
		Ind Avg Gas	Cert Gas	M-85	Cold Start	Hot Stab	Hot Start	Diurnal	Hot Soak	Running Losses	
01678-91-7	E-Cyclohexane	0.119	0.065	0.019	0.0000	0.0000	0.0000	0.0005	0.0019	0.0000	0.0002
00926-82-9	3,5-DM-Heptane	0.290	0.174	0.041	0.0003	0.0000	0.0000	0.0000	0.0009	0.0000	0.0001
00100-41-4	E-Benzene	3.283	1.989	0.498	0.0289	0.0000	0.0151	0.0084	0.0247	0.0000	0.0122
03074-71-3	2,3-DM-Heptane	0.073	0.048	0.012	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
00108-38-3	m&p-Xylene	7.537	4.703	1.177	0.0709	0.0072	0.0323	0.0211	0.0584	0.0000	0.0304
02216-34-4	4M-Octane	0.426	0.215	0.059	0.0036	0.0000	0.0009	0.0000	0.0000	0.0000	0.0010
02216-33-3	3M-Octane	0.406	0.208	0.058	0.0021	0.0000	0.0000	0.0000	0.0000	0.0000	0.0005
00100-42-5	Styrene	0.091	0.066	0.014	0.0056	0.0000	0.0000	0.0000	0.0000	0.0000	0.0013
00095-47-6	o-Xylene	2.691	1.710	0.420	0.0245	0.0000	0.0104	0.0062	0.0206	0.0000	0.0099
00124-11-8	1-Nonene	0.105	0.119	0.016	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
00627-20-3	c-2-Pentene	0.358	0.218	0.049	0.0007	0.0000	0.0000	0.0050	0.0057	0.0018	0.0018
00513-35-9	2M-2-Butene	1.032	0.617	0.142	0.0063	0.0000	0.0013	0.0167	0.0199	0.0047	0.0068
00542-92-7	Cyclopentadiene	0.003	0.002	0.000	0.0008	0.0000	0.0000	0.0000	0.0000	0.0000	0.0002
00075-83-2	2,2-DM-Butane	1.057	0.114	0.142	0.0034	0.0000	0.0058	0.0090	0.0103	0.0026	0.0056
00142-29-0	Cyclopentene	0.153	0.091	0.021	0.0000	0.0000	0.0000	0.0002	0.0010	0.0000	0.0001
00691-37-2	4M-1-Pentene	0.000	0.000	0.000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
00760-20-3	3M-1-Pentene	0.120	0.072	0.017	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
00287-92-3	Cyclopentane	0.208	0.111	0.030	0.0003	0.0000	0.0000	0.0014	0.0018	0.0000	0.0004
00079-29-8	2,3-DM-Butane	1.621	0.689	0.224	0.0104	0.0000	0.0098	0.0099	0.0158	0.0052	0.0078
01634-04-4	MTBE	0.000	0.000	0.000	0.0000	0.0000	0.0000	0.0019	0.0049	0.0000	0.0007
00691-38-3	4M-c-2-Pentene	0.000	0.000	0.000	0.0000	0.0000	0.0000	0.0000	0.0019	0.0000	0.0002
00107-83-5	2M-Pentane	4.870	1.537	0.675	0.0298	0.0127	0.0381	0.0315	0.0564	0.0181	0.0281
00674-76-0	4M-t-2-Pentene	0.132	0.081	0.018	0.0000	0.0000	0.0000	0.0000	0.0004	0.0000	0.0000
00096-14-0	3M-Pentane	2.422	0.975	0.338	0.0155	0.0044	0.0178	0.0147	0.0257	0.0071	0.0128
00763-29-1	2M-1-Pentene	0.237	0.141	0.036	0.0000	0.0000	0.0000	0.0000	0.0015	0.0000	0.0001
00592-41-6	1-Hexene	0.109	0.064	0.015	0.0000	0.0000	0.0000	0.0007	0.0006	0.0000	0.0001
00110-54-3	Hexane	2.457	0.697	0.343	0.0150	0.0059	0.0174	0.0138	0.0248	0.0051	0.0122
13269-52-8	t-3-Hexene	0.225	0.133	0.032	0.0000	0.0000	0.0000	0.0000	0.0005	0.0000	0.0000
07642-09-3	c-3-Hexene	0.000	0.000	0.000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
04050-45-7	t-2-Hexene	0.337	0.200	0.048	0.0002	0.0000	0.0000	0.0000	0.0012	0.0000	0.0002
00616-12-6	3M-t-2-Pentene	0.280	0.165	0.040	0.0011	0.0000	0.0000	0.0005	0.0024	0.0000	0.0005
00625-27-4	2M-2-Pentene	0.316	0.188	0.046	0.0000	0.0000	0.0000	0.0000	0.0010	0.0000	0.0001
01120-62-3	3M-Cyclopentene	0.313	0.217	0.053	0.0000	0.0000	0.0000	0.0034	0.0079	0.0010	0.0014
07688-21-3	c-2-Hexene	0.186	0.110	0.026	0.0000	0.0000	0.0000	0.0000	0.0004	0.0000	0.0000
00637-92-3	ETBE	0.000	0.000	0.000	0.0005	0.0000	0.0000	0.0003	0.0024	0.0000	0.0004
00590-35-2	2,2-DM-Pentane	0.344	0.203	0.051	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
00096-37-7	M-Cyclopentane	0.957	0.481	0.138	0.0066	0.0000	0.0047	0.0048	0.0096	0.0000	0.0037
00108-08-7	2,4-DM-Pentane	0.974	1.464	0.143	0.0069	0.0000	0.0051	0.0028	0.0044	0.0032	0.0039
00464-06-2	2,2,3-TM-Butane	0.023	0.022	0.001	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
00071-43-2	Benzene	1.776	0.689	0.300	0.0494	0.0459	0.0553	0.0192	0.0447	0.0058	0.0349
03404-61-3	3M-1-Hexene	0.022	0.007	0.002	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
00562-49-2	3,3-DM-Pentane	0.104	0.067	0.015	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
00110-82-7	Cyclohexane	0.195	0.079	0.028	0.0002	0.0000	0.0000	0.0000	0.0004	0.0000	0.0001
00591-76-4	2M-Hexane	1.478	1.923	0.211	0.0089	0.0000	0.0045	0.0039	0.0077	0.0020	0.0044
00565-59-3	2,3-DM-Pentane	1.478	1.923	0.211	0.0100	0.0000	0.0085	0.0046	0.0077	0.0046	0.0059
00110-83-8	Cyclohexene	0.026	0.015	0.004	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
00589-34-4	3M-Hexane	1.397	0.874	0.203	0.0100	0.0000	0.0076	0.0045	0.0078	0.0018	0.0051
02532-58-3	c-1,3-DM-Cyclopentane	0.311	0.155	0.046	0.0004	0.0000	0.0000	0.0000	0.0004	0.0000	0.0001
00822-50-4	t-1,2-DM-Cyclopentane	0.426	0.244	0.061	0.0012	0.0000	0.0000	0.0000	0.0006	0.0000	0.0003
00592-76-7	1-Heptene	0.000	0.000	0.000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
00540-84-1	2,2,4-TM-Pentane	3.341	4.700	0.481	0.0249	0.0246	0.0330	0.0164	0.0208	0.0200	0.0233
14686-14-7	t-3-Heptene	0.095	0.042	0.014	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
00142-82-5	Heptane	1.168	0.576	0.169	0.0065	0.0000	0.0043	0.0012	0.0052	0.0010	0.0030
00111-84-2	Nonane	0.280	0.175	0.042	0.0004	0.0000	0.0000	0.0000	0.0000	0.0000	0.0001
00098-82-8	i-PropBenzene	0.139	0.091	0.022	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
15869-87-1	2,2-DM-Octane	0.090	0.099	0.013	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
00100-52-7	Benzaldehyde	0.037	0.023	0.006	0.0011	0.0000	0.0000	0.0000	0.0000	0.0000	0.0003
04032-94-4	2,4-DM-Octane	0.158	0.112	0.025	0.0039	0.0000	0.0014	0.0000	0.0015	0.0000	0.0012
00103-65-1	n-PropBenzene	0.713	0.441	0.111	0.0046	0.0000	0.0000	0.0000	0.0008	0.0000	0.0011
00620-14-4	1M-3E-Benzene	2.116	1.290	0.320	0.0192	0.0000	0.0054	0.0018	0.0100	0.0000	0.0064
00622-96-8	1M-4E-Benzene	0.924	0.566	0.140	0.0085	0.0000	0.0010	0.0006	0.0023	0.0000	0.0024
00108-67-8	1,3,5-TM-Benzene	1.092	0.663	0.168	0.0088	0.0000	0.0012	0.0000	0.0018	0.0000	0.0024
00611-14-3	1E-2M-Benzene	0.751	0.444	0.117	0.0068	0.0000	0.0010	0.0000	0.0009	0.0000	0.0018
00095-63-6	1,2,4-TM-Benzene	2.912	1.768	0.441	0.0232	0.0000	0.0055	0.0034	0.0114	0.0000	0.0077
00124-18-5	Decane	0.128	0.091	0.017	0.0005	0.0000	0.0000	0.0000	0.0000	0.0000	0.0001

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Appendix. Continued.

CAS #	Compound	FUELS			EXHAUST EMISSIONS			EVAPORATIVE EMISSIONS			COMPSTE
		Ind Avg Gas	Cert Gas	M-85	Cold Start	Hot Stab	Hot Start	Diurnal	Hot Soak	Running Losses	
00135-98-8	s-ButBenzene	0.073	0.061	0.011	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
05161-04-6	1M-4-i-ButBenzene	0.027	0.022	0.001	0.0000	0.0000	0.0016	0.0000	0.0000	0.0000	0.0002
00576-73-8	1,2,3-TM-Benzene	0.612	0.389	0.088	0.0047	0.0000	0.0000	0.0000	0.0005	0.0000	0.0011
00496-11-7	Indan	0.399	0.233	0.057	0.0017	0.0000	0.0000	0.0000	0.0000	0.0000	0.0004
00141-93-5	1,3-DE-Benzene	0.263	0.183	0.036	0.0002	0.0000	0.0000	0.0000	0.0000	0.0000	0.0001
00105-05-5	1,4-DE-Benzene	0.105	0.065	0.015	0.0019	0.0000	0.0000	0.0000	0.0000	0.0000	0.0004
00104-51-8	n-ButBenzene	0.608	0.377	0.086	0.0063	0.0000	0.0000	0.0000	0.0000	0.0000	0.0015
00135-01-3	1,2-DE-Benzene	0.270	0.178	0.037	0.0004	0.0000	0.0000	0.0000	0.0000	0.0000	0.0001
01120-21-4	Undecane	0.092	0.063	0.015	0.0014	0.0000	0.0000	0.0000	0.0000	0.0000	0.0003
00095-93-2	1,2,4,5-TetM-Benzene	0.254	0.156	0.037	0.0002	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
00527-53-7	1,2,3,5-TetM-Benzene	0.353	0.222	0.050	0.0010	0.0000	0.0000	0.0000	0.0000	0.0000	0.0002
00488-23-3	1,2,3,4-TetM-Benzene	0.223	0.139	0.033	0.0002	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
00091-20-3	Naphthalene	0.476	0.301	0.073	0.0032	0.0000	0.0000	0.0000	0.0000	0.0000	0.0007
00112-40-3	Dodecane	0.111	0.071	0.016	0.0031	0.0000	0.0000	0.0000	0.0000	0.0000	0.0007
00067-56-1	Methanol	0.000	0.000	85.034							
00107-02-8	Acrolein				0.0012	0.0012	0.0000				0.0005
00067-64-1	Acetone				0.0025	0.0286	0.0094				0.0066
00123-38-6	Propionaldehyde				0.0004	0.0053	0.0011				0.0011
00123-73-9	Crotonaldehyde				0.0004	0.0029	0.0023				0.0009
00123-72-8	n-Butyraldehyde				0.0004	0.0001	0.0000				0.0001
00078-93-3	Butanone				0.0005	0.0079	0.0003				0.0015
00110-62-3	Pentanaldehyde				0.0000	0.0000	0.0000				0.0000
00104-87-0	p-Tolualdehyde				0.0005	0.0103	0.0046				0.0025
00066-25-1	Hexanaldehyde				0.0000	0.0000	0.0000				0.0000
TOTAL		88.638	92.256	98.313	0.9888	0.9606	0.9896	0.9969	0.9964	1.0001	0.9883

^aExample tailpipe, evaporative, and composite hydrocarbon emissions speciation using industry average gasoline and projected for a light-duty vehicle fleet for a given location and future year. Data adapted from the Auto/Oil Program database.